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MW-1: A CERTIFIED REFERENCE IRON ORE

H.F. STEGER, W.S. BOWMAN AND R. SUTARNO

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MINERALS RESEARCH PROGRAM
MINERAL SCIENCES LABORATORIES

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MW-1: A CERTIFIED REFERENCE IRON ORE

by

H.F. Steger*, W.S. Bowman** and R. Sutarno*

SYNOPSIS

A 256-kg sample of an iron ore concentrate, MW-1, from Mount Wright, Quebec was prepared as a compositional reference material. MW-1 was screened to pass 82 μm, blended in one lot, bottled in 200-g units and tested for homogeneity by X-ray fluorescence and chemical methods.

In a "free-choice" round-robin analytical program, 15 laboratories contributed results for one or more of twelve constituents. Eight of these were ultimately certified and their recommended values are: Fe - 66.08%; Fe(II) - 1.36%; SiO_2 - 4.60%; Al_2O_3 - 0.30%; CaO - 0.054%; MgO - 0.032%; P - 0.011%; and K - 0.011%. Provisional values for the other four are: TiO_2 - 0.13%; Mn - 0.016%; S - 0.011% and Na - 0.011%.

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*Research Scientists and **Technologist, Mineral Sciences Laboratories, CANMET, Energy, Mines and Resources Canada, Ottawa.

Note: Major contributions to the certification of MW-1 were also made by other staff members of the Mineral Sciences Laboratories.

MW-1: MINERAI DE RÉFÉRENCE DE FER

par

H.F. Steger*, W.S. Bowman** et R. Sutarno*

SYNOPSIS

Un échantillon de 256-kg de concentré de minerai de fer, MW-1, provenant de Mount Wright, Québec, a été préparé comme matériau de référence de composition déterminée. Le MW-1 a été tamisé à 82 µm, mélangé en lot de minerai, embouteillé en unités de 200 g et soumis à des essais d'homogénéité par la méthode de fluorescence X et par des méthodes chimiques.

En vertu d'un programme analytique de "libre choix", 15 laboratoires ont soumis des resultats sur chacun des deux flacons de MW-1 pour un de douze constituants ou plus dont huit ort été finalement certifiés. Leurs valeurs recommandées sont: Fe - 66,08%; Fe(II) - 1,36%; SiO_2 - 4,60%; Al_2O_3 - 0,30%; CaO - 0,054%; MgO - 0,032%; P - 0,011%; et K - 0,011%. Les valeurs provisoires pour les quatre autres constituants sont: TiO_2 - 0,13%; Mn - 0,016%; S - 0,011%; et Na - 0,011%.

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*Chercheurs scientifiques et **Technologue, Laboratoires des sciences minérales, CANMET, Energie, Mines et Ressources Canada, Ottawa.

Nota: D'autres membres des Laboratoires des sciences minérales ont aussi contribué à la certification du MW-1.

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INTRODUCTION

The preparation, characterization and certification of iron ore concentrate MW-1 is part of the continuing endeavour of the Canadian Certified Reference Materials Project (CCRMP) to provide compositional reference ores, concentrates and related products typical of Canadian deposits and not, in general, available from other sources for use in analytical laboratories associated with mining, metallurgy and the earth sciences. Other reference materials certified by CCRMP are described in a catalogue available from CANMET, Energy, Mines and Resources Canada, Ottawa (1).

MW-1 was prepared as a reference material on request from the Canadian Advisory Committee to ISO Technical Committee 102 on iron ores for use in the analytical laboratories associated with the iron ore mining and steelmaking industries. This material differs from other reference iron ores presently available in that it is essentially a specular hematite. An interlaboratory program was conducted to obtain results for total iron, ferrous iron, silicon, aluminum, titanium, calcium, magnesium, manganese, phosphorus, sulphur, sodium and potassium from 15 laboratories using analytical methods of their choice for all elements except sodium and potassium for which the method of ISO/TC 102/SC 2(2) was requested. The results should therefore be representative of the "state-of-the-art" of the analysis of these elements in these two related industries.

NATURE AND PREPARATION

The raw material for MW-1 was donated in January 1980 by Quebec Cartier Mining Company and is typical iron ore concentrate from Mount Wright, Quebec. It is essentially specular hematite with minor to trace amounts of quartz, iron silicates and ilmenite.

MW-1 was passed through a 82-μm screen in August 1980. The powdered ore weighing approximately 256 kg was tumbled for 9 h in a 570-L conical blender and bottled in 200-g units. MW-1 was found sufficiently homogeneous in iron, silicon and titanium contents by an X-ray fluorescence technique performed at CANMET and in silicon and sodium contents by chemical methods at Lakefield Research of Canada Limited, under contract to CANMET, to proceed with its certification as a reference material. The results of the homogeneity testing of MW-1 are shown in Appendix A.

The particle size analysis is given in Table 1.

Table 1 - Particle size analysis (wet screen)

Size of fraction (μm)	wt %*
-104 + 74	9.0
- 74 + 46	17.6
- 46	73.4

* Mean of duplicate determinations

INTERLABORATORY PROGRAM FOR CERTIFICATION

The laboratories that participated in the certification program for MW-1 are listed alphabetically in Appendix B. Each was assigned a code number which bears no relation to its alphabetical order.

Each laboratory was requested to contribute three replicate results on each of two bottles for as many as possible of total iron, ferrous iron, silicon, aluminum, magnesium, calcium, phosphorus, sulphur, manganese, titanium, sodium and potassium by methods of its choice, except for sodium and potassium for which the method of ISO/TC 102/SC 2 was requested. Participating laboratories were also requested to dry MW-1 at 105°C for 2 h (3). Some laboratories, however, deviated from the request for six results or contributed results by more than one method. When the latter occurred, each set was considered statistically independent. The recommended values for total iron, ferrous iron, silicon dioxide, aluminum oxide, calcium oxide, magnesium oxide, phosphorus and potassium are reported in Table 2. Provisional values for titanium dioxide, manganese, sodium and sulphur are reported in Table 3. Statistical and methodological information is presented in Tables 4, 5 and 6.

Table 2 - Recommended values and related statistics (outliers excluded)

Constituent	No. of laboratories	No. of sets of results	Total No. of results	Overall mean	95% CL High	95% CL Low	σ_A
				wt %			
Fe (total)	13	16	104	66.08	66.14	66.02	0.06
Fe (ferrous)	9	10	74	1.36	1.40	1.31	0.03
SiO_2	14	16	108	4.60	4.66	4.53	0.03
Al_2O_3	14	15	90	0.30	0.31	0.29	0.007
CaO	12	13	84	0.054	0.057	0.051	0.003
MgO	13	15	92	0.032	0.034	0.029	0.001
P	11	12	76	0.011	0.012	0.010	0.0006
K	12	13	78	0.011	0.012	0.010	0.0005

Table 3 - Provisional values and related statistics (outliers excluded)

Constituent	No. of laboratories	No. of sets of results	Total No. of results	Overall mean	σ_A
				wt %	
TiO_2	12	14	86	0.13	0.004
Mn	14	17	106	0.016	0.0005
S	12	13	85	0.011	0.0005
Na	12	13	83	0.011	0.0007

Table 4a - Analytical results, laboratory means and standard deviations for total iron

						MEAN	S.D.
LAB- 1 (TITR)	66.08	66.07	66.06	66.03	66.10	66.0733	.0175
	66.05						
LAB- 3 (TITR)	65.73	66.00	66.15	65.95	66.18	65.9717	.1777
	65.82						
LAB- 3 (TITR)	65.84	65.98	65.96	65.90	66.04	65.9350	.0720
	65.89						
LAB- 4 (TITR)	66.07	66.04	66.01	66.08	66.06	66.0533	.0250
	66.06						
LAB- 5 (TITR)	66.16	66.20	66.21	66.12	66.14	66.1750	.0409
	66.22						
LAB- 8 (TITR)	66.15	66.15	66.23	66.15	66.15	66.1633	.0327
	66.15						
LAB- 9 (TITR)	66.17	66.26	66.22	66.17	66.10	66.2400	.1474
	66.52						
LAB- 9 (TITR)	65.90	65.82	65.80	65.84	66.01	65.8600	.0832
	65.79						
LAB-10 (TITR)	66.0629	66.0629	66.1493	66.0660		66.0854	.0430
LAB-10 (TITR)	66.0040	65.9942	66.0088	66.1082	66.0454	66.0621	.0475
	66.0772	66.0487	66.1221	66.0485	66.0527		
	66.0657	66.1252	66.0347	66.0388	66.0534		
	66.1667						
LAB-11 (TITR)	66.29	66.29	66.25	66.18	66.18	66.2333	.0509
	66.21						
LAB-12 (TITR)	66.175	66.080	66.186	66.176	66.030	66.1347	.0642
	66.161						
LAB-13 (TITR)†	65.55	65.63	65.56	65.56	65.80	65.6400	.1002
	65.72						
LAB-15 (TITR)	65.90	65.92	66.05	66.02	65.95	65.9717	.0585
	65.99						
LAB-16 (TITR)	66.00	66.02	66.02	66.00	66.02	66.0067	.0163
	65.98						
LAB-17 (TITR)	66.08	66.26	66.15	66.27	66.13	66.2150	.1174
	66.40						
LAB-18 (TITR)	66.12	66.15	66.13	66.16	66.18	66.1583	.0331
	66.21						

†Outlying set

Table 4b - Analytical results, laboratory means and standard deviations for ferrous iron

						MEAN	S.D.
LAB- 1 (TITR)	1.33 1.31	1.34	1.31	1.34	1.40	1.3533	.0388
LAB- 3 (TITR)	1.379 1.351	1.331	1.380	1.316	1.354	1.3602	.0255
LAB- 3 (TITR)	1.319 1.356	1.343	1.369	1.349	1.363	1.3496	.0178
LAB- 4 (TITR)	1.29 1.34	1.30	1.29	1.29	1.29	1.3000	.0200
LAB- 5 (TITR)†	0.91 0.96	0.95	0.96	0.92	0.95	.9417	.0214
LAB- 8 (TITR)	1.38 1.38	1.36	1.38	1.38	1.40	1.3800	.0126
LAB- 9 (TITR)	1.26 1.28	1.24	1.27	1.29	1.24	1.2633	.0207
LAB-10 (TITR)	1.473 1.473 1.473 1.473	1.356 1.431 1.356 1.356	1.386 1.401 1.401 1.431	1.517 1.467 1.433 1.467	1.368 1.400 1.379 1.410	1.4226	.0483
LAB-11 (TITR)	1.31 1.35	1.35	1.35	1.31	1.31	1.3300	.0219
LAB-17 (TITR)	1.32 1.45	1.34	1.32	1.34	1.39	1.3600	.0510
LAB-18 (TITR)	1.30 1.29	1.27	1.29	1.29	1.30	1.2900	.0110

†Outlying set

Table 4c - Analytical results, laboratory means and standard deviations

for silicon dioxide

						MEAN	S.D.
LAKFLD (AA)	4.58	4.62	4.60	4.62	4.60	4.6033	.0151
	4.60						
LAB- 1 (GRAV)	4.56	4.55	4.57	4.60	4.59	4.5817	.0264
	4.62						
LAB- 3 (GRAV)	4.525	4.543	4.516	4.543	4.549	4.5393	.0161
	4.560						
LAB- 3 (GRAV)	4.536	4.529	4.520	4.517	4.526	4.5242	.0076
	4.517						
LAB- 4 (GRAV)	4.47	4.48	4.49	4.48	4.50	4.4833	.0103
	4.48						
LAB- 5 (GRAV)	4.54	4.54	4.58	4.58	4.58	4.5700	.0245
	4.60						
LAB- 8 (AA)	4.59	4.51	4.68	4.61	4.76	4.6283	.0847
	4.62						
LAB- 9 (GRAV)	4.41	4.39	4.45	4.43	4.45	4.4267	.0234
	4.43						
LAB-10 (COLOR)	4.792	4.759	4.693	4.828	4.777	4.7720	.0540
	4.747	4.737	4.868	4.729	4.846		
	4.777	4.711					
LAB-10 (AA)	4.768	4.734	4.671	4.768	4.734	4.7342	.0568
	4.671	4.827	4.734	4.671	4.827		
	4.734	4.671					
LAB-11 (GRAV)	4.57	4.61	4.53	4.53	4.60	4.5583	.0412
	4.51						
LAB-12 (GRAV)	4.6845	4.6795	4.6688	4.6950	4.6787	4.6813	.0085
	4.6814						
LAB-13 (AA)	4.61	4.63	4.61	4.62	4.61	4.6133	.0103
	4.60						
LAB-15	4.520	4.484	4.548	4.606		4.5395	.0515
LAB-16 (GRAV)†	5.03	5.03	5.04	5.04		5.0350	.0058
LAB-17 (GRAV)	4.09*	4.58	4.60	4.53	4.49	4.4900	.1523
	4.47	4.58	4.62	4.45	4.49		
LAB-18 (COLOR)	4.41	4.42	4.39	4.41	4.39	4.3883	.0402
	4.31						

†Outlying set
*Outlying result

Table 4d - Analytical results, laboratory means and standard deviations for aluminum oxide

						MEAN	S.D.
LAB- 1 (AA)	0.30	0.30	0.29	0.31	0.29	.2983	.0075
	0.30						
LAB- 3 (AA)	0.329	0.335	0.330	0.335	0.311	.3248	.0118
	0.309						
LAB- 3 (AA)	0.325	0.324	0.327	0.323	0.324	.3245	.0014
	0.324						
LAB- 4 (AA)	0.306	0.294	0.282	0.298	0.293	.2932	.0085
	0.286						
LAB- 5 (AA)	0.31	0.30	0.30	0.29	0.29	.2983	.0075
	0.30						
LAB- 8 (AA)	0.29	0.29	0.30	0.31	0.29	.2967	.0082
	0.30						
LAB- 9 (AA)	0.384*	0.308	0.266	0.308	0.272	.3027	.0437
	0.278						
LAB-10 (AA)	0.329	0.331	0.319	0.331	0.327	.3262	.0060
	0.322	0.334	0.327	0.315	0.329		
	0.331	0.319					
LAB-11 (AA)	0.26	0.26	0.26	0.26	0.25	.2583	.0041
	0.26						
LAB-12 (AA)	0.3112	0.3166	0.3051	0.3082	0.3066	.3085	.0048
	0.3031						
LAB-13 (AA)	0.331	0.333	0.331	0.285	0.331	.3237	.0190
	0.331						
LAB-15	0.297	0.289	0.289	0.293		.2920	.0038
LAB-16 (COLOR)	0.30	0.30	0.30	0.30		.3000	0.0000
LAB-17 (AA)	0.299	0.303	0.302	0.300	0.299	.2987	.0050
	0.289						
LAB-18 (AA)	0.264	0.272	0.272	0.272	0.272	.2718	.0048
	0.279						

*Outlying result

Table 4e - Analytical results, laboratory means and standard deviations for titanium dioxide

						MEAN	S.D.
LAB- 1 (AA)	0.134	0.130	0.134	0.132	0.130	.1313	.0024
	0.128						
LAB- 3 (COLOR)	0.124	0.124	0.122	0.121	0.121	.1225	.0014
	0.123						
LAB- 3 (COLOR)	0.113	0.113	0.115	0.113	0.116	.1143	.0015
	0.116						
LAB- 4 (COLOR)	0.124	0.118	0.116	0.118	0.123	.1200	.0032
	0.121						
LAB- 5 (AA)	0.13	0.16	0.16	0.16	0.16	.1500	.0155
	0.13						
LAB- 8 (AA)	0.14	0.13	0.16	0.14	0.14	.1417	.0098
	0.14						
LAB- 9 (COLOR)	0.149	0.155	0.162	0.169	0.150	.1570	.0076
	0.157						
LAB-10 (AA)	0.142	0.137	0.136	0.142	0.137	.1388	.0025
	0.142	0.142	0.137	0.139	0.138		
	0.137	0.136					
LAB-10 (AA)	0.137	0.140	0.141	0.141	0.139	.1395	.0013
	0.139	0.139	0.140				
LAB-11 (COLOR)†	0.18	0.18	0.18	0.18	0.18	.1800	0.0000
	0.18						
LAB-12 (COLOR)	0.1208	0.1201	0.1193	0.1221	0.1209	.1207	.0009
	0.1211						
LAB-15	0.1226	0.1203				.1215	.0016
LAB-16 (COLOR)	0.125	0.125	0.125	0.125		.1250	0.0000
LAB-17 (AA)	0.137	0.140	0.137	0.138	0.138	.1375	.0016
	0.135						
LAB-18 (AA)	0.100	0.106	0.100	0.100	0.113	.1053	.0064
	0.113						

†Outlying set

Table 4f - Analytical results, laboratory means and standard deviations for calcium oxide

						MEAN	S.D.
LAB- 1 (AA)	0.059	0.057	0.057	0.057	0.064	.0592	.0029
	0.061						
LAB- 3 (AA)	0.057	0.055	0.066*	0.057	0.054	.0573	.0044
	0.055						
LAB- 3 (AA)	0.061	0.061	0.063	0.060	0.061	.0602	.0027
	0.055						
LAB- 4 (AA)	0.0487	0.0477	0.0478	0.0473	0.0487	.0489	.0021
	0.0530						
LAB- 5 (AA)	0.056	0.053	0.053	0.054	0.066	.0575	.0056
	0.063						
LAB- 8 (AA)	0.06	0.04	0.04	0.06	0.06	.0533	.0103
	0.06						
LAB- 9 (AA)†	0.109*	0.091	0.088	0.092	0.087	.0925	.0083
	0.088						
LAB-10 (AA)	0.0547	0.0477	0.0526	0.0547	0.0490	.0523	.0033
	0.0541	0.0563	0.0477	0.0541	0.0547		
	0.0477	0.0541					
LAB-10 (AA)	0.0549	0.0495	0.0571	0.0565	0.0495	.0540	.0036
	0.0564	0.0560	0.0487	0.0580	0.0552		
	0.0494	0.0573					
LAB-11 (AA)†	0.09	0.08	0.09	0.08	0.09	.0850	.0055
	0.08						
LAB-12 (AA)	0.0530	0.0538	0.0525	0.0524	0.0530	.0529	.0005
	0.0528						
LAB-13 (AA)†	0.035	0.032	0.031	0.036	0.031	.0330	.0023
LAB-15	0.0641	0.0623	0.0632			.0632	.0009
LAB-16 (AA)	0.053	0.053	0.053	0.053		.0530	0.0000
LAB-17 (AA)	0.056	0.057	0.060	0.056	0.056	.0568	.0016
	0.056						
LAB-18 (AA)	0.042	0.041	0.041	0.041	0.042	.0415	.0005
	0.042						

†Outlying set
*Outlying result

Table 4g - Analytical results, laboratory means and standard deviations for magnesium oxide

						MEAN	S.D.
LAB- 1 (AA)	0.035	0.033	0.035	0.035	0.036	.0348	.0010
	0.035						
LAB- 3 (AA)	0.033	0.031	0.030	0.031	0.030	.0310	.0011
	0.031						
LAB- 3 (AA)	0.035	0.035	0.035	0.036	0.034	.0348	.0008
	0.034						
LAB- 4 (AA)	0.0271	0.0267	0.0268	0.0268	0.0277	.0270	.0004
	0.0270						
LAB- 5 (AA)	0.032	0.030	0.030	0.030	0.030	.0308	.0013
	0.033						
LAB- 8 (AA)	0.04	0.04	0.04	0.05	0.05	.0433	.0052
	0.04						
LAB- 9 (AA)	0.051*	0.036	0.035	0.035	0.035	.0378	.0065
	0.035						
LAB-10 (AA)	0.0298	0.0362	0.0298	0.0327	0.0284	.0312	.0024
	0.0312	0.0305	0.0312				
LAB-10 (AA)	0.0316	0.0277	0.0323	0.0319	0.0299	.0313	.0013
	0.0330	0.0313	0.0292	0.0328	0.0311		
	0.0298	0.0325					
LAB-11 (AA)†	0.07	0.06	0.06	0.05	0.05	.0583	.0075
	0.06						
LAB-12 (AA)	0.0266	0.0270	0.0267	0.0305	0.0295	.0281	.0016
	0.0284						
LAB-13 (AA)	0.0307	0.0308	0.0298	0.0300	0.0307	.0305	.0004
	0.0307						
LAB-15	0.0317	0.0325	0.0325			.0322	.0005
LAB-16 (AA)	0.030	0.030	0.030	0.030		.0300	.0000
LAB-17 (AA)	0.028	0.028	0.028	0.031	0.031	.0290	.0015
	0.028						
LAB-18 (AA)	0.027	0.029	0.027	0.029	0.028	.0278	.0010
	0.027						

†Outlying set
*Outlying result

Table 4h - Analytical results, laboratory means and standard deviations for manganese

						MEAN	S.D.
LAB- 1 (AA)	0.014	0.015	0.015	0.014	0.014	.0142	.0008
	0.013						
LAB- 3 (AA)	0.016	0.017	0.015	0.015	0.015	.0155	.0008
	0.015						
LAB- 3 (AA)	0.015	0.015	0.015	0.015	0.015	.0150	.0000
	0.015						
LAB- 4 (AA)	0.0157	0.0152	0.0149	0.0148	0.0148	.0151	.0003
	0.0152						
LAB- 5 (AA)	0.016	0.016	0.016	0.016	0.016	.0160	0.0000
	0.016						
LAB- 8 (AA)	0.02	0.02	0.02	0.02	0.02	.0200	0.0000
	0.02						
LAB- 9 (AA)	0.017	0.016	0.018	0.017	0.018	.0173	.0008
	0.018						
LAB- 9 (COLOR)	0.016	0.017	0.016	0.016	0.015	.0160	.0006
	0.016						
LAB-10 (AA)	0.0174	0.0176	0.0174	0.0176	0.0174	.0175	.0001
	0.0176	0.0174	0.0176				
LAB-10 (AA)	0.0178	0.0177	0.0173	0.0176	0.0174	.0175	.0002
	0.0172	0.0178	0.0174	0.0174	0.0176		
	0.0175	0.0171					
LAB-11 (AA)	0.019	0.019	0.020	0.018	0.019	.0188	.0008
	0.018						
LAB-12 (AA)	0.0168	0.0171	0.0172	0.0183	0.0175	.0174	.0005
	0.0174						
LAB-13 (AA)	0.0125	0.0123	0.0120	0.0120	0.0122	.0122	.0002
	0.0122						
LAB-15	0.0165	0.0160	0.0168	0.0155		.0162	.0006
LAB-16 (COLOR)	0.018	0.018	0.018	0.018		.0180	0.0000
LAB-17 (AA)	0.019	0.019	0.019	0.018	0.019	.0188	.0004
	0.019						
LAB-18 (AA)	0.012	0.012	0.012	0.012	0.013	.0122	.0004
	0.012						

Table 4i - Analytical results, laboratory means and standard deviations for phosphorus

						MEAN	S.D.
LAB- 1 (COLOR)	0.012	0.011	0.012	0.011	0.012	.0117	.0005
	0.012						
LAB- 3 (COLOR)	0.0113	0.0109	0.0109	0.0113	0.0109	.0110	.0002
	0.0109						
LAB- 3 (COLOR)	0.0117	0.0117	0.0117	0.0117	0.0117	.0117	.0000
	0.0117						
LAB- 4 (TITR)	0.0119	0.0129	0.0124	0.0114	0.0129	.0122	.0007
	0.0114						
LAB- 5 (COLOR)	0.008	0.008	0.008	0.008	0.008	.0080	0.0000
	0.008						
LAB- 9 (COLOR)	0.0120	0.0115	0.0120	0.0116	0.0120	.0119	.0002
	0.0120						
LAB-10 (AA)	0.0102	0.0111	0.0097	0.0099	0.0114	.0104	.0010
	0.0086	0.0104	0.0113	0.0090	0.0104		
	0.0117	0.0112					
LAB-11 (TITR)	0.010	0.010	0.011	0.009	0.010	.0098	.0008
	0.009						
LAB-15	0.016	0.014	0.013	0.013		.0140	.0014
LAB-16 (COLOR)	0.013	0.013	0.013	0.013		.0130	.0000
LAB-17 (GRAV)	0.0094	0.0097	0.0103	0.0103	0.0100	.0100	.0005
	0.0098	0.0091	0.0107				
LAB-18 (COLOR)	0.0131	0.0129	0.0134	0.0129	0.0129	.0131	.0002
	0.0133						

Table 4j - Analytical results, laboratory means and standard deviations for sulphur

						MEAN	S.D.
LAB- 1 (COMB)	0.010	0.010	0.010	0.010	0.010	.0100	0.0000
	0.010						
LAB- 3 (COMB)	0.010	0.010	0.009	0.009	0.009	.0094	.0005
	0.010	0.009	0.009				
LAB- 3 (COMB)	0.009	0.009	0.010	0.010	0.009	.0096	.0005
	0.010	0.010					
LAB- 4 (COMB)	0.0155	0.0150	0.0145	0.0140	0.0143	.0145	.0007
	0.0135						
LAB- 5 (COMB)†	0.020	0.021	0.021	0.021	0.021	.0208	.0004
	0.021						
LAB- 9 (COMB)	0.016	0.015	0.015	0.014	0.014	.0148	.0008
	0.015						
LAB-10 (COMB)	0.0110	0.0112	0.0111	0.0105	0.0123	.0113	.0007
	0.0120	0.0124	0.0112	0.0110	0.0115		
	0.0121	0.0111	0.0098	0.0114	0.0111		
	0.0109						
LAB-11 (COMB)	0.008	0.008	0.009	0.008	0.009	.0083	.0005
	0.008						
LAB-12 (COMB)	0.0100	0.0097	0.0102	0.0100	0.0100	.0100	.0002
	0.0103						
LAB-13 (COMB)	0.0088	0.0079	0.0088	0.0098	0.0089	.0089	.0006
	0.0090						
LAB-15	0.0179	0.0170	0.0170	0.0170		.0172	.0005
LAB-16 (COMB)	0.012	0.011				.0115	.0007
LAB-17 (COMB)	0.0098	0.0099	0.0103	0.0105	0.0103	.0102	.0003
	0.0105						
LAB-18 (COMB)	0.0120	0.0125	0.0120	0.0120	0.0120	.0122	.0003
	0.0125						

†Outlying set

Table 4k - Analytical results, laboratory means and standard deviations for sodium

						MEAN	S.D.
LAKFLD (AA)	0.0118	0.0115	0.0112	0.0119	0.0112	.0114	.0004
	0.0110						
LAB- 1 (AA)	0.011	0.011	0.012	0.012	0.011	.0113	.0005
	0.011						
LAB- 3 (AA)	0.0166	0.0128	0.0140	0.0121	0.0122	.0133	.0018
	0.0118						
LAB- 3 (AA)	0.0120	0.0126	0.0127	0.0114	0.0123	.0120	.0006
	0.0112						
LAB- 4 (AA)	0.0115	0.0106	0.0108	0.0107	0.0108	.0109	.0003
	0.0109						
LAB- 5 (AA)	0.007	0.008	0.006	0.005	0.005	.0060	.0013
	0.005						
LAB- 9 (AA)	0.010	0.009	0.009	0.009	0.009	.0092	.0004
	0.009						
LAB-10 (AA)	0.0118	0.0119	0.0113	0.0115	0.0119	.0117	.0002
	0.0113	0.0117	0.0119	0.0115	0.0118		
	0.0119	0.0115					
LAB-11 (AA)	0.007	0.006	0.007	0.007	0.007	.0067	.0005
	0.006						
LAB-12 (AA)	0.0114	0.0116	0.0117	0.0121	0.0115	.0116	.0003
	0.0113						
LAB-13 (AA)	0.0134	0.0129	0.0128	0.0133	0.0137	.0133	.0004
	0.0136						
LAB-15 (AA)	0.0075	0.0091	0.0105	0.0099	0.0100	.0094	.0012
LAB-16 (AE)†	0.004	0.004				.0040	0.0000
LAB-17 (AE)†	0.023	0.021	0.019	0.019	0.018	.0197	.0020
	0.018						
LAB-18 (AA)	0.013	0.014	0.014	0.015	0.014	.0140	.0006
	0.014						

†Outlying set

Table 4i - Analytical results, laboratory means and standard deviations for potassium

						MEAN	S.D.
LAB- 1 (AA)	0.009	0.010	0.010	0.009	0.009	.0095	.0005
	0.010						
LAB- 3 (AA)	0.0141*	0.0122	0.0118	0.0114	0.0120	.0122	.0010
	0.0118						
LAB- 3 (AA)	0.0110	0.0115	0.0113	0.0110	0.0113	.0113	.0003
	0.0117						
LAB- 4 (AA)	0.0101	0.0092	0.0086	0.0097	0.0090	.0093	.0005
	0.0091						
LAB- 5 (AA)	0.015	0.014	0.013	0.014	0.013	.0137	.0008
	0.013						
LAB- 9 (AA)	0.010	0.010	0.010	0.010	0.010	.0100	0.0000
	0.010						
LAB-10 (AA)	0.0111	0.0111	0.0110	0.0109	0.0114	.0111	.0002
	0.0110	0.0114	0.0111	0.0110	0.0116		
	0.0111	0.0110					
LAB-11 (AA)†	0.007	0.008	0.007	0.007	0.008	.0073	.0005
	0.007						
LAB-12 (AA)	0.0103	0.0103	0.0105	0.0104	0.0106	.0104	.0001
	0.0104						
LAB-13 (AA)	0.0101	0.0101	0.0100	0.0100	0.00966	.0100	.0002
	0.0101						
LAB-15 (AA)	0.0122	0.0116	0.0112	0.0116	0.0109	.0115	.0005
LAB-16 (AE)	0.012	0.012				.0120	0.0000
LAB-17 (AE)	0.013	0.012	0.010	0.010	0.010	.0108	.0013
	0.010						
LAB-18 (AA)	0.013	0.012	0.012	0.013	0.012	.0125	.0005
	0.013						

†Outlying set
*Outlying result

STATISTICAL TREATMENT OF ANALYTICAL RESULTS

DETECTION OF OUTLIERS

Any sets of results obviously suspect for methodological reasons were rejected. Sets having unusually high variances were examined and any individual outlying results were deleted. Also, the sets of results whose means differed by more than twice the overall standard deviation from the initially calculated mean value were not used in subsequent computations to avoid biasing the statistics. All results that were rejected are identified in Table 4.

CONFIRMATION OF HOMOGENEITY USING INTERLABORATORY RESULTS

Using the t-test at the 5% significance level, a comparison was made of the reported results for both bottles from each set (4). The number of sets where the null hypothesis of no difference between bottles was rejected are reported in Table 5. The percentage of sets rejected is appreciably lower than that found in previous CCRMP interlaboratory programs. The significance of these instances of between-bottle inhomogeneity detected by the t-test with respect to real physical inhomogeneity has been discussed elsewhere by the Coordinator CCRMP (5).

Table 5 - Results of t-tests between bottles at the 5% significance level (outliers excluded)

Constituent	Total No. of sets	No. of sets rejecting t-test
Fe (total)	16	2
Fe (ferrous)	10	1
SiO_2	16	1
Al_2O_3	14	0
CaO	11	0
MgO	13	1
TiO_2	12	0
Mn	14	0
P	10	0
S	11	1
Na	12	0
K	11	0

ESTIMATION OF CONSENSUS VALUES AND 95% CONFIDENCE LIMITS

A one-way analysis of variance technique was used to estimate the consensus value and its variance. This approach considers the results of the described certification program to be only one sampling out of a universal set of results. The analytical data were assumed to fit the model (4).

$$x_{ij} = \mu + y_i = e_{ij}$$

where x_{ij} = the j^{th} result in set i,
μ = the true consensus value,
y_i = the discrepancy between the mean of the results in set i ($\bar{x}_i.$) and μ, and
e_{ij} = the discrepancy between x_{ij} and $\bar{x}_i.$

It is assumed that both y_i and e_{ij} are normally distributed with means of zero and variances of ω^2 and σ^2, respectively. The significance of ω^2 is detected by comparing the ratio of between-set mean squares to within-set mean squares with the F statistic at the 95% confidence level and with the appropriate degrees of freedom.

The consensus value of the assumed model is estimated by the overall mean $\bar{x}..$:

$$\bar{x}.. = \sum_i^k \sum_j^{n_i} x_{ij} \Big/ \sum_i^k n_i$$

where n_i = the number of results in set i, and
k = the number of sets.

The value of σ_2 is estimated by s_1^2 which is given by:

$$s_1^2 = \sum_i^k \sum_j^{n_i} (x_{ij} - \bar{x}_i.)^2 \Big/ \sum_i^k n_i - k$$

The value of ω^2 is estimated by:

$$\omega^2 = (s_2^2 - s_1^2) \Big/ \frac{1}{k-1} \left(\sum_i^k n_i - \sum_i^k n_i^2 / \sum_i^k n_i \right)$$

where

$$s_2^2 = \sum_i^k n_i (\bar{x}_i. - \bar{x}..)^2 \Big/ k-1$$

The variance of the overall mean is given by:

$$V[\bar{\bar{x}}..] = \left(\sum_i^k n_i^2 / (\sum_i^k n_i)^2\right) \omega^2 + \left(1/\sum_i^k n_i\right) \sigma^2$$

and the 95% confidence limits for $\bar{\bar{x}}..$ are

$$\bar{\bar{x}}.. \pm t_{0.975,\ (k-1)} \sqrt{V[\bar{\bar{x}}..]}$$

where t is from the Student's t probability distribution function (4).

It should be noted that 95% confidence limits denote that if the certification program were performed 100 times, the overall mean in 95 would fall within the prescribed limits.

The average within-set standard deviation, σ_A, is a measure of the average within-bottle precision as determined by the analytical methods used. The implication exists therefore that a laboratory using a method of average or better reproducibility should obtain individual results for a given certified element with a precision that is at least comparable to the reported value of σ_A.

Table 6a - Summary of analytical methods for total iron (outliers excluded)

Finish	Decomposition, separation, etc.	Laboratory	No. of results	Fe (wt %)
Titrimetry	Method ISO/TC 102 N585E; HCl; residue treated with H_2SO_4 + HF to dryness and fused with Na_2CO_3; $SnCl_2$ reduction followed with $HgCl_2$; finish with $K_2Cr_2O_7$	3a, 17	12	66.09
	One or more of HCl + $HClO_4$ + HF + $SnCl_2$; $SnCl_2$ reduction followed with $HgCl_2$; finish with $K_2Cr_2O_7$	CANMET (a), 1, 4, 8	40	66.15
	Fusion with one or both of Na_2O_2 + Na_2CO_3; taken up in dilute HCl; $SnCl_2$ reduction followed by $HgCl_2$; finish with $K_2Cr_2O_7$	CANMET (b), 3b, 12	18	65.98
	Fusion with Na_2O_2 + Na_2CO_3; reduction with Jones Reductor; finish with $K_2Cr_2O_7$	5	6	66.18
	Fusion with Na_2O_2; taken up in dilute HCl; silver reduction; finish with $K_2Cr_2O_7$	10b, 16	22	66.05
	Decomposition as per ISO/TC 102 N585E; reduction with $SnCl_2$ followed by slight excess of $TiCl_3$ which is oxidized with $HClO_4$; finish with $K_2Cr_2O_7$	15	6	65.97

Table 6b - Summary of analytical methods for ferrous iron (outliers excluded)

Finish	Decomposition, separation, etc.	Laboratory	No. of results	Fe(II) (wt %)
Titrimetry	Dissolution with one or more of HCl + HF + H_2CO_3 under CO_2 gas; finish with $K_2Cr_2O_7$	CANMET 1, 4, 8, 10, 11, 17, 18	62	1.36
	Dissolution with HCl under CO_2; finish with cerate	3a, 3b	12	1.36

Table 6c - Summary of analytical methods for SiO_2 (outliers excluded)

Finish	Decomposition, separation, etc.	Laboratory	No. of results	SiO_2 (wt %)
Gravimetry	One or more of HCl + $HClO_4$; fusion of insolubles with either Na_2CO_3 or Na_2CO_3; dehydration; weigh before and after SiF_4 volatilization	3a, 3b, 5	18	4.54
	One or both of HCl + $HClO_4$; dehydration; weigh before and after SiF_4 volatilization	CANMET 4, 11, 12, 17	33	4.54
	JIS M-8214	1	6	4.58
Atomic absorption	HCl; fusion of insolubles with Na_2O_2; taken up in dilute HCl	13, LKFLD	12	4.61
	Fusion with $LiBO_2$; taken up in dilute HNO_3	8	6	4.63
	Fusion with $Na_2B_4O_7$; taken up in dilute HCl	10b	12	4.73
Colorimetry	Fusion with $Na_2B_4O_7$; taken up in HNO_3; molybdenum blue finish	10a	12	4.77
	Fusion with $NaKCO_3$ + $Na_2B_4O_7$; taken up in H_2SO_4; molybdenum	18	5	4.40
?	No information	15	4	4.54

Table 6d - Summary of analytical methods for Al_2O_3 (outliers excluded)

Finish	Decomposition, separation, etc.	Laboratory	No. of results	Al_2O_3 (wt %)
Atomic absorption	One or more of HCl + HF + $HClO_4$; fusion of insolubles with Na_2CO_3 + B_2O_3 or $Na_2B_4O_7$	4, 11	12	0.276
	HCl; fusion of insolubles with Na_2CO_3 + B_2O_3; volatilization of Si as SiF_4	3a, 3b	12	0.325
	HCl; fusion of insolubles with either Na_2O_2 or Na_2CO_3	12, 13	11	0.319
	HCl + $HClO_4$; insolubles treated with HF + $HClO_4$; iron removed by mercury cathode electrolysis	CANMET	5	0.286
	HCl + HNO_3; Si volatilized as SiF_4	17	6	0.299
	Fusion with either $Na_2B_4O_7$ or $NaKCO_3$ + $Na_2B_4O_7$; taken up in dilute HCl	10, 18	18	0.308
	Fusion with Na_2O_2; taken up in dilute HCl	5	6	0.298
	Fusion with $LiBO_2$; taken up in dilute HNO_3	8	6	0.297
	JIS M-8222	1	6	0.298
Colorimetry	STELCO chromazurol 'S' method	16	4	0.300
?	No information	15	4	0.292

Table 6e - Summary of analytical methods for TiO_2 (outliers excluded)

Finish	Decomposition, separation etc.	Laboratory	No. of results	TiO_2 (wt %)
Atomic absorption	One or more of HCl + HNO_3 + HF + H_2SO_4; fusion of insolubles	10a, 10b	20	0.139
	HCl + HNO_3; Si volatilized as SiF_4	17	6	0.138
	Fusion with one of $LiBO_2$, Na_2O_2 or $NaKCO_3$ + $Na_2B_4O_7$; taken up in HCl	5, 8, 18	18	0.132
	JIS M-8219	1	6	0.131
Colorimetry	HCl; fusion of insolubles with Na_2CO_3; $HClO_4$ + HF to volatilize SiF_4; colour development with chromotropic acid	3a, 3b, 4	18	0.119
	Fusion with $K_2S_2O_7$; taken up in H_2SO_4; colour development with H_2O_2	CANMET	6	0.157
	Fusion with $Na_2B_2O_7$ + Na_2CO_3; taken up in HCl; Fe(III) reduced with ascorbic acid; colour development with dianti-pyrylmethane	12	6	0.121
	"STELCO" method; colour development with chromotropic acid	16	4	0.125
?	No information	15	2	0.122

Table 6f - Summary of analytical methods for CaO (outliers excluded)

Finish	Decomposition, separation, etc.	Laboratory	No. of results	CaO (wt %)
Atomic absorption	One or more of HCl + HF + $HClO_4$; fusion of insolubles with Na_2CO_3 + B_2O_3 or $Na_2B_4O_7$ or Na_2O_2	4, 10b, 12	24	0.053
	HCl; fusion of insolubles with Na_2CO_3 + B_2O_3; $HClO_4$ + HF to volatilize SiF_4	3a, 3b	11	0.058
	HF + HCl	5	6	0.058
	HCl + HNO_3; volatilize SiF_4	17	6	0.057
	JIS M-8221	1	6	0.059
	HCl + HNO_3; insolubles treated with HF + H_2SO_4; insolubles fused with Na_2CO_3	16	4	0.053
	Fusion with $LiBO_2$; taken up in HNO_3; La_2O_3 added	8	6	0.053
	Fusion with $Na_2B_4O_7$; taken up in HCl; La_2O_3 added	10a	12	0.052
	Fusion with $NaKCO_3$ + $Na_2B_4O_7$; taken up in HCl	18	6	0.042
	HCl + HNO_3; insolubles treated with HF + H_2SO_4; insolubles fused with Na_2CO_3	16	4	0.053
?	No information	15	3	0.063

Table 6g - Summary of analytical methods for MgO (outliers excluded)

Finish	Decomposition, separation, etc.	Laboratory	No. of results	MgO (wt %)
Atomic absorption	One or more of HCl + HF + $HClO_4$; fusion of insolubles with Na_2CO_3 + B_2O_3 or $Na_2B_4O_7$ or Na_2O_2	4, 10b, 12	30	0.030
	HCl; fusion of insolubles with Na_2CO_3 + B_2O_3; $HClO_4$ + HF to volatilize SiF_4	3a, 3b	12	0.033
	HF + HCl	5	6	0.031
	HCl + $HClO_4$; insolubles with HF + $HClO_4$; iron removed by mercury cathode electrolysis	CANMET	5	0.035
	HCl + HNO_3; volatilize SiF_4; La_2O_3 added	17	6	0.029
	JIS M-8222	1	6	0.035
	HCl + HNO_3; insolubles treated with HF + H_2SO_4; insolubles fused with Na_2CO_3	16	4	0.030
	Fusion with $LiBO_2$; taken up in HNO_3	8	6	0.043
	Fusion with $Na_2B_4O_7$; taken up in HCl	10a	8	0.031
	Fusion with $NaKCO_3$ + $Na_2B_4O_7$; taken up in HCl	18	6	0.028
?	No information	15	3	0.032

Table 6h - Summary of analytical methods for phosphorus

Finish	Decomposition, separation, etc.	Laboratory	No. of results	P (wt %)
Titrimetry	HCl + HF; fusion of insolubles with Na_2CO_3 + B_2O_3; ammonium phosphomolybdate precipitated and redissolved in NaOH; excess NaOH titrated with HNO_3	4	6	0.0122
	HCl + $SnCl_2$; HF to volatilize SiF_4; ammonium phosphomolybdate precipitated; zinc reduction and titration with permanganate	11	6	0.0098
Atomic absorption	HCl + $SnCl_2$; insolubles with HF + H_2SO_4; phosphorus precipitated as ammonium phosphomolybdate; re-dissolved in NH_4OH; molybdenum determined and phosphorus calculated by theoretical relationship	10	12	0.0104
Colorimetry	HCl; fusion of residue with Na_2CO_3 + B_2O_3; H_2SO_4 + HF to volatilize SiF_4; molybdenum blue colour development	3a, 3b	12	0.0114
	HCl + $HClO_4$; insolubles treated with HCl + HF + $HClO_4$; add $Na_2S_2O_7$ and $Bi_2(SO_4)_3$; molybdenum blue colour development	CANMET	6	0.0119
	JIS M-8216; molybdenum blue colour development	1	6	0.0117
	Molybdenum blue colour development	16	4	0.0130
	$HClO_4$; phosphovandomolybdate extraction into iso-amyl alcohol	5	6	0.0080
	HF + $HClO_4$; ammonium phosphomolybdate extraction into iso-butyl alcohol	18	6	0.0131
Gravimetry	HCl + HNO_3 + $HClO_4$; quinoline phosphomolybdate precipitated	17	8	0.0100
?	No information	15	4	0.0140

Table 6i - Summary of analytical methods for Mn (outliers excluded)

Finish	Decomposition, separation, etc.	Laboratory	No. of results	Mn (wt %)
Atomic absorption	One or more of HCl + HF + $HClO_4$; fusion of insolubles with Na_2CO_3 + B_2O_3 or $Na_2B_4O_7$ or Na_2O_2	4, 10b, 11, 12, 13	36	0.016
	HCl; fusion of insolubles with Na_2CO_3 + B_2O_3; $HClO_4$ + HF to volatilize SiF_4	3a, 3b	12	0.015
	HF + HCl	5	6	0.016
	HCl + $HClO_4$; insolubles with HF + $HClO_4$	CANMET (a)	6	0.017
	HCl + HNO_3; volatilize SiF_4	17	6	0.019
	JIS M-8215	1	6	0.014
	Fusion with $LiBO_2$; taken up in HNO_3	8	6	0.020
	Fusion with $Na_2B_4O_7$; taken up in HCl	10a	8	0.0175
	Fusion with $NaKCO_3$ + $Na_2B_4O_7$; taken up in HCl	18	6	0.12
Colorimetry	HCl + $HClO_4$; insolubles with HF + $HClO_4$; iron removed by mercury cathode electrolysis; manganese oxidized to permanganate	CANMET (b)	6	0.016
	Oxidation to permanganate	16	4	0.018
?	No information	15	4	0.0162

Table 6j - Summary of analytical methods for sulphur (outliers excluded)

Finish	Decomposition, separation, etc.	Laboratory	No. of results	S (wt %)
Titrimetry	Combustion; SO_2 absorbed by $AgNO_3$ solution; titrated with NaOH	CANMET	6	0.0148
Iodometry	Combustion; titration with KI + KIO_3	3a, 3b, 4, 10, 11, 12, 17, 18	61	0.0107
	Combustion; JIS M-8217	1	6	0.0100
Infrared-spectrometry	Combustion; SO_2 measured by infrared spectrometry	13	6	0.0089
Conductometry	Combustion; SO_2 measured conductometrically; details not stated	16	2	0.0115
?	No information	15	4	0.0172

Table 6k - Summary of analytical methods for sodium (outliers excluded)

Finish	Decomposition, separation, etc.	Laboratory	No. of results	Na (wt %)
Atomic absorption	ISO TC 102/256E: HCl + HF; taken up in HCl	CANMET 1, 3a, 3b 12, 13, 15, LKFLD	47	0.0115
	HCl + HF; taken up in HCl	4, 5, 18	18	0.0103
	HCl + HF + $SnCl_2$; taken up in HCl	10	12	0.0117
	Tri-acid decomposition; volatilization of SiF_4	11	6	0.0067

Table 6l - Summary of analytical methods for potassium (outliers excluded)

Finish	Decomposition, separation, etc.	Laboratory	No. of results	K (wt %)
Atomic absorption	ISO TC 102N/256E: HCl + HF; taken up in HCl	CANMET 1, 3a, 3b 12, 13, 15	40	0.0106
	HCl + HF; taken up in HCl	4, 5, 18	18	0.0118
	HCl + HF + $SnCl_2$; taken up in HCl	10	12	0.0111
Flame emission	ISO TC 102N/256E: HCl + HF; taken up in HCl	17	6	0.0108
?	No information	16	2	0.0120

CRITERION FOR CERTIFICATION

The ratio of the between-laboratory to the within-laboratory standard deviation, σ_B/σ_A, where

$$\sigma_B = \sqrt{\sum_i^k (\bar{x}_{i\cdot} - \bar{x}_{\cdot\cdot})^2/k-1}$$

is a measure of the quality of the certification data for the reference materials of CCRMP (6). The acceptable upper limit for σ_B/σ_A is 3 for all elements except uranium for which an upper limit of 2 is more realistic.

The criterion for the certification of an element in a reference material is RP, the percentage of sets of results that must be rejected to give a value of σ_B/σ_A equal to or less than the acceptable upper limit. RP cannot exceed 15%.

It is CCRMP's practice to exclude the results of laboratories having unusually large within-laboratory variance from the calculation of σ_A in order not to unduly favor certifiability. Conversely, the results of laboratories having zero variance have been excluded from the calculation of σ_A. Table 7 reports the values of σ_B/σ_A and RP for the constituents in MW-1. Clearly, titanium dioxide, manganese, sulphur and sodium do not satisfy the criterion for certifiability.

Table 7 - Statistics for certifiability

Constituent	σ_B/σ_A	RP (%)
Fe (total)	2.31	0.0
Fe (ferrous)	1.85	9.1
SiO_2	2.84	11.8
Al_2O_3	2.50	6.7
TiO_2	2.94	20.0
CaO	2.68	12.5
MgO	2.47	12.5
P	2.74	0.0
Mn	2.68	17.6
Na	2.47	26.7
K	2.59	7.1
S	2.52	28.6

DISCUSSION

Table 6 is a summary of a methodological classification of accepted analytical results where there is a clear-cut distinction between types of methods in decomposition, separation and determination steps. It can be deduced therein that most laboratories determined two or more of silicon, aluminum, calcium, magnesium, titanium and manganese on the same subsample. All laboratories determined sodium and potassium on the same subsample.

Figure 1 illustrates the plots of the relative frequency against the content interval for all results for the constituents in MW-1. The observed distributions are in general acceptable but those for manganese and sulphur seem to indicate a lack of consensus between laboratories.

The inability to certify MW-1 for sodium is surprising in view of the availability of the well-established ISO Method 256, the use of which did however lead to the certification of potassium. Interestingly, 8 of the 15 laboratories associated with the iron ore and steel industry did not specifically use this method. The mean of the seven laboratories that did employ ISO method 256 was 0.0117% which differs only slightly from the provisional value of 0.0109%. A similar situation had been encountered previously for sodium and potassium in reference iron ore SCH-1 (7,8).

INFORMATION VALUES FOR COPPER, NICKEL AND ZINC

Laboratory 10 voluntarily submitted 28 results for copper and nickel and 24 results for zinc by three methods for each constituent. The means are in µg/g: Cu - 11, Ni - 900, Zn - 16.

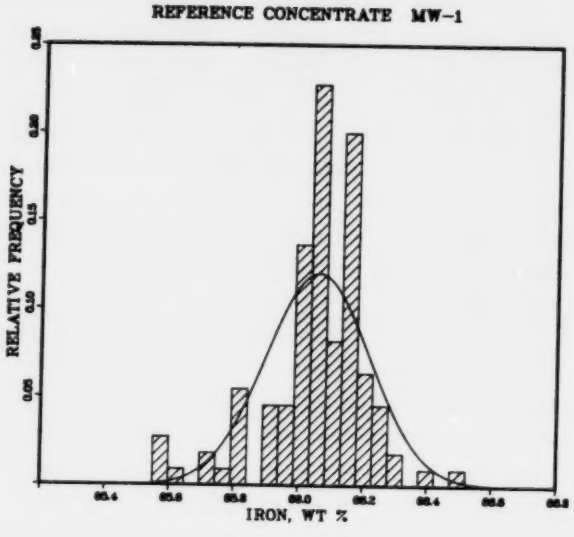

Fig. 1a - Histogram for total iron

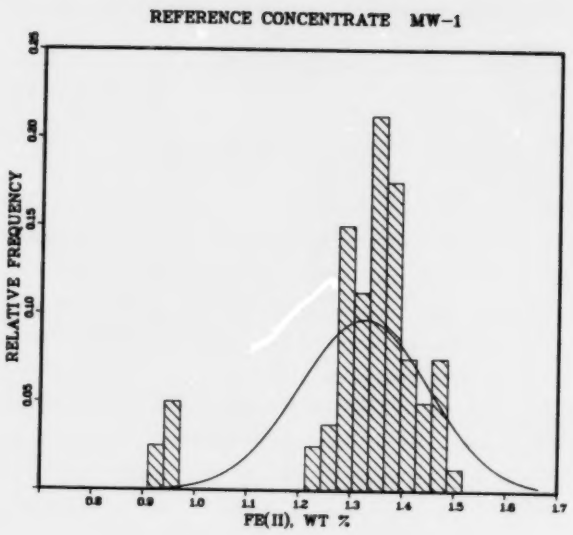

Fig. 1b - Histogram for ferrous iron

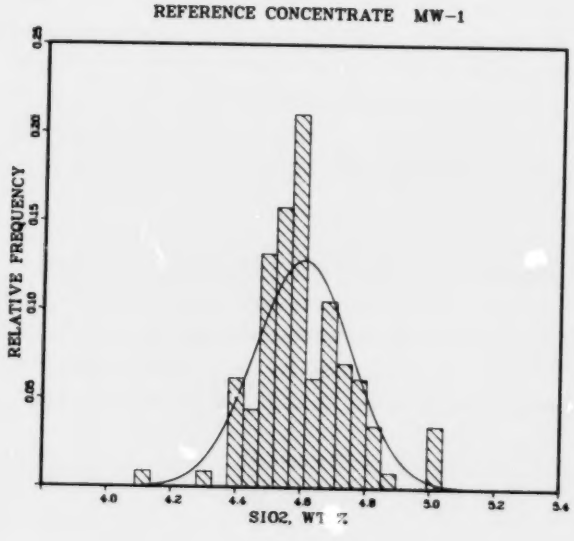

Fig. 1c - Histogram for silicon dioxide

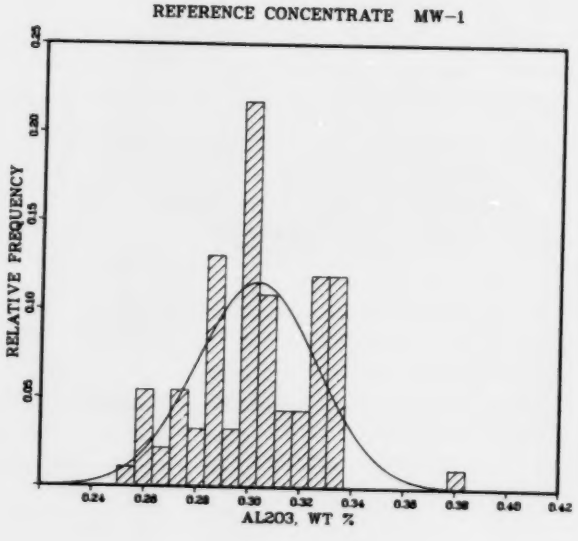

Fig. 1d - Histogram for aluminum oxide

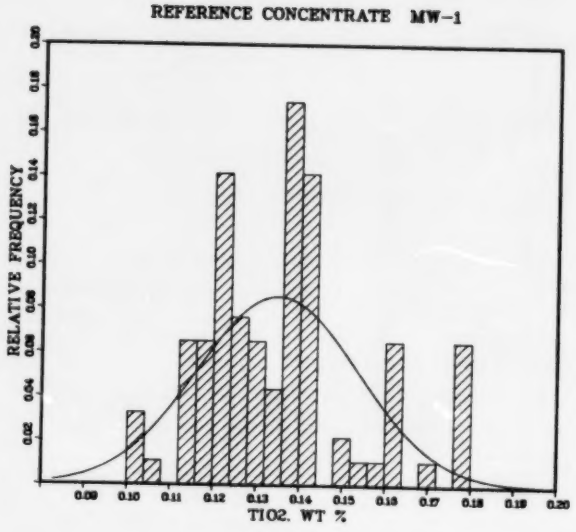

Fig. 1e - Histogram for titanium dioxide

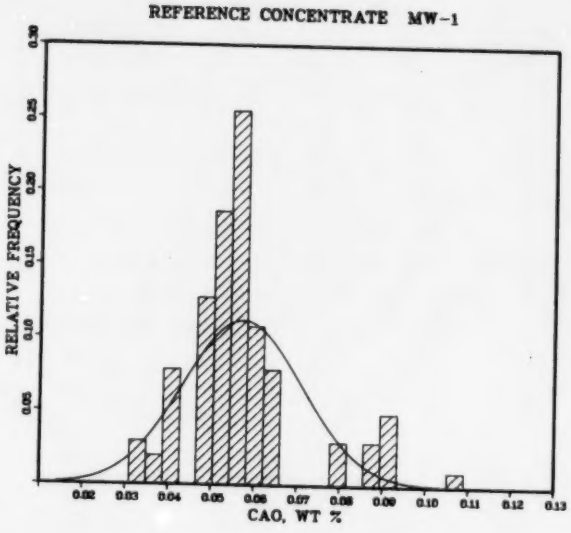

Fig. 1f - Histogram for calcium oxide

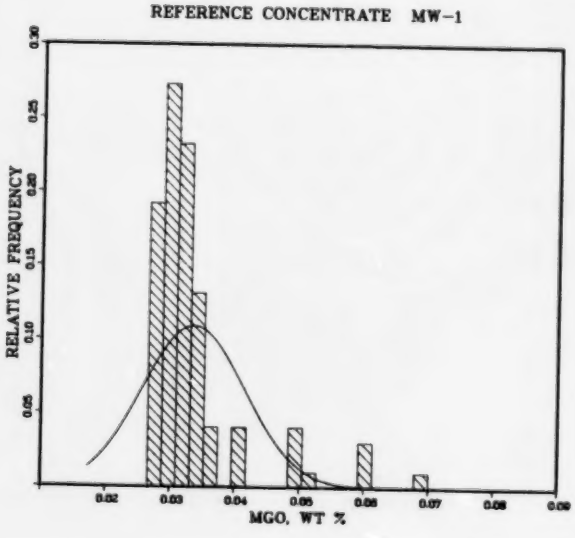

Fig. 1g - Histogram for magnesium oxide

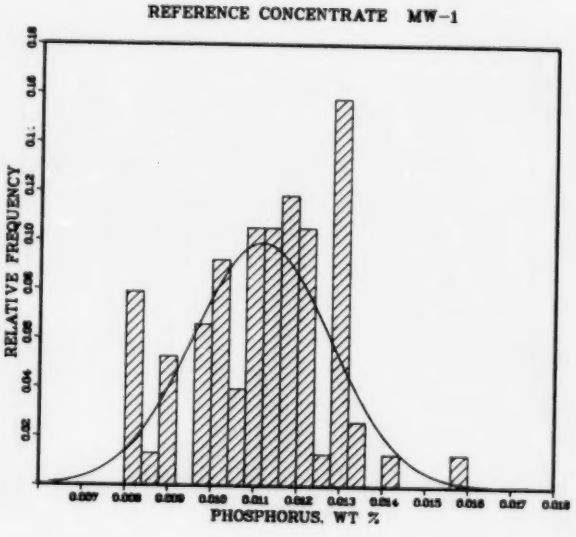

Fig. 1h - Histogram for phosphorus

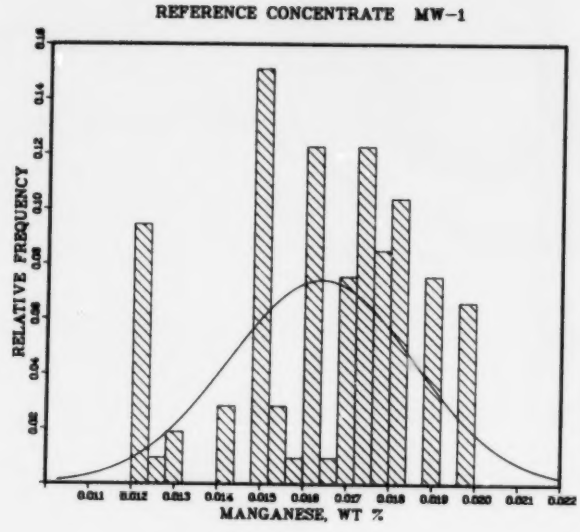

Fig. 1i - Histogram for manganese

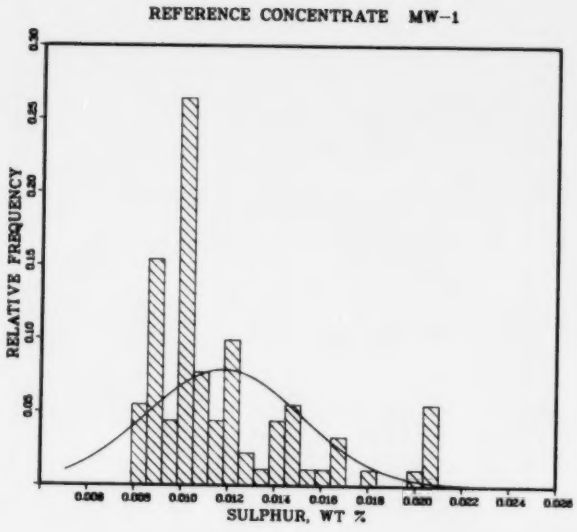

Fig. 1j - Histogram for sulphur

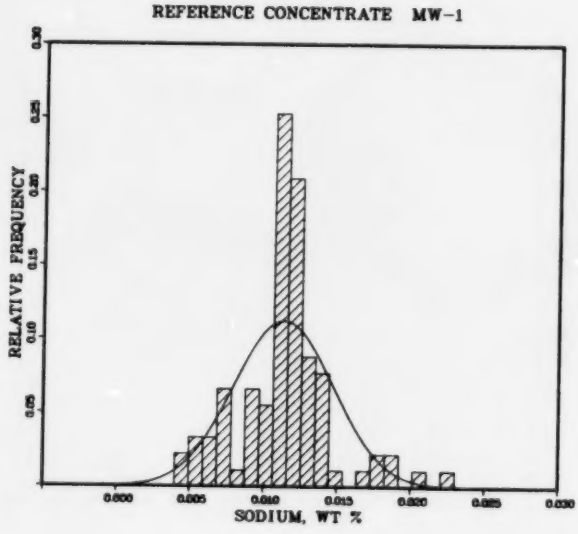

Fig. 1k - Histogram for sodium

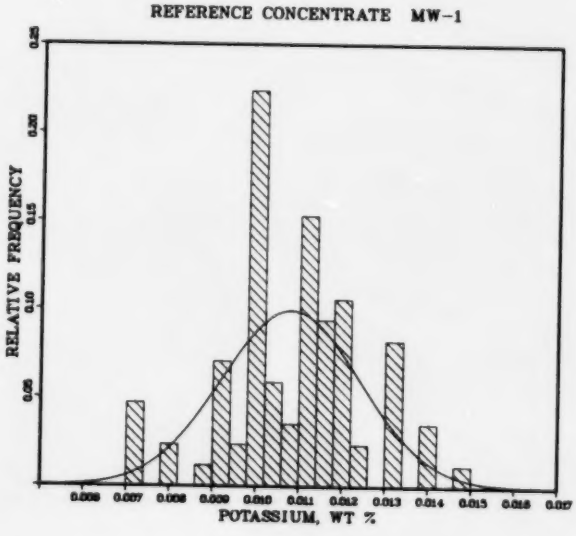

Fig. 1ℓ - Histogram for potassium

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APPENDIX A

HOMOGENEITY TESTING OF MW-1

HOMOGENEITY TESTING OF MW-1

The homogeneity of MW-1 was tested at CANMET by analyzing in triplicate, 12 bottles for iron, silicon and titanium by an X-ray fluorescence technique using pressed-powder pellets. These bottles were selected as follows: the stock of 1180 bottles was divided into 11 lots of 99 and a twelfth lot of 91 bottles. The code number of the first bottle was selected at random out of the first lot. The code numbers of the other 11 bottles were given by the code of the preceding bottle plus 99. The results are reported in Table 8.

The homogeneity of MW-1 was also examined by Lakefield Research of Canada Limited by analyzing in triplicate, 15 bottles for silicon and sodium using chemical methods. For sodium, ISO Method 256 was used (2). The bottles consisted of the 12 selected above for analysis at CANMET and three additional bottles selected at random from the stock of MW-1. The results are reported in Table 9.

A one-way analysis of variance technique was used to assess the homogeneity (4). This involves comparing the ratio of the between-bottle to within-bottle mean square with the F statistic at the 95% level of probability. No evidence of bottle-to-bottle inhomogeneity was found for either analytical procedure.

Table 8a - Confirmation of homogeneity of MW-1 for iron (X-ray fluorescence)

Bottle No.	Fe (counts) Individual			Mean
43	2,098,311	2,096,375	2,118,429	2,104,371
142	2,078,432	2,079,046	2,086,241	2,081,240
241	2,102,442	2,090,577	2,090,548	2,096,322
340	2,090,924	2,090,161	2,095,439	2,092,175
439	2,080,367	2,092,319	2,073,793	2,082,160
538	2,093,351	2,104,577	2,098,473	2,098,800
637	2,102,993	2,102,900	2,089,729	2,098,539
736	2,068,124	2,090,849	2,098,423	2,085,799
835	2,089,218	2,094,041	2,094,668	2,092,642
934	2,098,665	2,095,595	2,063,735	2,085,998
1033	2,074,474	2,091,852	2,091,963	2,086,096
1132	2,098,579	2,111,333	2,095,617	2,101,843
		Overall mean		2,092,165

Analysis of variance table for iron

Source of variation	Degrees of freedom	Mean square
Between bottles	11	5.561×10^8
Within bottles	24	2.981×10^8
Total	35	

Calculated F statistic = 1.866

F.95 (11,24) = 2.20

Null hypothesis of no difference between bottles is accepted for iron

Table 8b - Confirmation of homogeneity of MW-1 for silicon (X-ray fluorescence)

Bottle No.	Si (counts) Individual			Mean
43	13,005	13,018	12,772	12,932
142	16,214	12,417	12,381	13,670
241	12,929	12,775	12,760	12,821
340	12,873	12,910	12,985	12,923
439	12,529	12,710	12,017	12,419
538	12,621	12,492	12,798	12,637
637	12,959	12,345	12,687	12,663
736	12,391	12,430	12,338	12,386
835	12,836	12,230	12,472	12,512
934	12,836	12,681	12,393	12,637
1033	12,670	12,433	12,893	12,665
1132	12,363	12,709	12,829	12,634
		Overall mean		12,742

Analysis of variance table for silicon

Source of variation	Degrees of freedom	Mean square
Between bottles	11	1.036×10^6
Within bottles	24	1.347×10^6
Total	35	

Calculated F statistic = 0.769

F.95 (11,24) = 2.20

Null hypothesis of no difference between bottles is accepted for silicon

Table 8c - Confirmation of homogeneity of MW-1 for titanium (X-ray fluorescence)

Bottle No.	Fe (counts) Individual			Mean
43	65,988	68,349	69,848	68,061
142	73,155	69,352	67,766	70,091
241	67,250	67,897	68,405	67,851
340	68,114	68,691	68,467	68,424
439	66,200	68,245	66,417	66,954
538	68,126	69,168	69,684	68,992
637	70,913	69,300	67,330	69,181
736	66,917	65,109	68,540	66,855
835	67,540	69,879	65,740	67,720
934	68,165	63,387	66,629	66,060
1033	68,079	67,574	65,890	67,181
1132	65,689	71,356	69,455	68,500
		Overall mean		67,989

Analysis of variance table for titanium

Source of variation	Degrees of freedom	Mean square
Between bottles	11	1.156×10^7
Within bottles	24	9.883×10^6
Total	35	

Calculated F statistic = 1.169

F.95 (11,24) = 2.20

Null hypothesis of no difference between bottles is accepted for titanium

Table 9a - Confirmation of homogeneity of MW-1 for silicon (chemical method)

Bottle No.	Si (mean %) Individual			Mean
43	2.16	2.11	2.12	2.12
142	2.15	2.14	2.18	2.16
241	2.16	2.11	2.15	2.14
307	2.14	2.16	2.15	2.15
340	2.18	2.12	2.16	2.15
439	2.16	2.15	2.15	2.15
538	2.15	2.18	2.17	2.17
552	2.16	2.18	2.17	2.17
637	2.16	2.12	2.17	2.15
736	2.16	2.15	2.16	2.16
831	2.11	2.20	2.18	2.13
835	2.13	2.17	2.16	2.15
934	2.18	2.18	2.15	2.17
1033	2.17	2.13	2.16	2.15
1132	2.17	2.16	2.16	2.16
		Overall mean		2.155

Analysis of variance table for silicon

Source of variation	Degrees of freedom	Mean square
Between bottles	14	3.514×10^{-4}
Within bottles	30	4.933×10^{-4}
Total	44	

Calculated F statistic = 0.712

F.95 (14,30) = 2.037

Null hypothesis of no difference between bottles is accepted for silicon

Table 9b - Confirmation of homogeneity of MW-1 for sodium (chemical method)

Bottle No.	Na (mean %) Individual			Mean
43	0.0118	0.0114	0.0113	0.0115
142	0.0118	0.0112	0.0113	0.0114
241	0.0119	0.0116	0.0112	0.0116
307	0.0118	0.0115	0.0112	0.0115
340	0.0117	0.0113	0.0111	0.0114
439	0.0119	0.0112	0.0110	0.0114
538	0.0118	0.0115	0.0111	0.0115
552	0.0117	0.0115	0.0110	0.0114
637	0.0117	0.0113	0.0113	0.0114
736	0.0120	0.0110	0.0113	0.0114
831	0.0117	0.0115	0.0114	0.0115
835	0.0117	0.0115	0.0111	0.0114
934	0.0116	0.0118	0.0112	0.0115
1033	0.0114	0.0114	0.0112	0.0113
1132	0.0120	0.0116	0.0116	0.0117
		Overall mean		0.0115

Analysis of variance table for sodium

Source of variation	Degrees of freedom	Mean square
Between bottles	14	2.975×10^{-8}
Within bottles	30	1.033×10^{-7}
Total	44	

Calculated F statistic = 0.288

F.95 (14,30) = 2.037

Null hypothesis of no difference between bottles is accepted for sodium

APPENDIX B

PARTICIPATING LABORATORIES

PARTICIPATING LABORATORIES

CANMET, Energy, Mines and Resources
Mineral Sciences Laboratories,
Ottawa, Ontario

Dofasco, Inc.
Hamilton, Ontario
W. Van de Vrande

HOGANAS A.B.
Metallurgical Division
Hoganas, Sweden
W. Zensch

INCO Metals Company
J. Roy Gordon Research Laboratory
Mississauga, Ontario
V.J. Zatka

Iron Ore Company of Canada
Special Laboratory
Sept-Iles, Quebec
S.H. Ng

Ledoux and Company
Teaneck, New Jersey
S. Kallmann

Lerch Brothers Incorporated
Hibbing, Minnesota
R. Carlson

LUOSSAVAARA-KIRUNAVAARA AB,
Central Research Laboratory
Kiruna, Sweden
S.O. Eriksson

Ministère de l'Energie et des Ressources
Direction de l'Analyse et du Contrôle
Gouvernement du Québec
Sainte-Foy, Québec
M. Pichette

Stelco Incorporated
Hilton Works
Hamilton, Ontario
O.P. Bhargava

United States Steel Corporation
Analytical Chemistry Division
Research Laboratory
Monroeville, Pennsylvania
L.M. Melnick

United States Steel Corporation
Minerals Beneficiation Division
Research Laboratory
Coleraine, Minnesota
R.L. Bleifuss